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Speciation of trimethyllead in rainwater by gas chromatography–mass spectrometry after ethylation with sodium tetraethylborate Comparison with other alkylation methods

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Abstract

This paper describes an analytical procedure to determine Me_3Pb^+ in aqueous solution. The method consists of ethylation of Me_3Pb^+ with $NaBEt_4$ in the presence of a small volume of hexane, and keeping an excess of Pb^{2+}. So, in only one step, the ethylation, the extraction and the concentration of the analyte are carried out. The organic extract is analyzed by GC–MS in the selected ion monitoring mode, using Me_4Pb as the internal standard. The different variables which affect the process – pH, volume of hexane and $NaBEt_4$ concentration – are optimized. Possible degradation compounds as well as the number of interferences are compared to the buthylation method through Grignard reaction. The method is applied to the analysis of an artificial rainwater solution as part of an international interlaboratory exercise, and the results obtained are discussed and compared with that given by buthylation method. © 1997 Elsevier Science B.V.

Keywords: Water analysis; Environmental analysis; Organolead compounds; Lead; Alkyllead compounds

1. Introduction

Ionic alkyllead compounds are products of degradation of tetraalkyllead (R_4Pb) which are mainly used as gasoline additives. Despite the fact that the use of leaded gasoline has decreased, their concentrations in the urban environment remain high and it is of extreme importance to establish the alkyllead concentration in the environment [1–3].

All these compounds have more profound physiological effects and show higher toxicity than inorganic lead, due to their good solubility in lipids and their good absorption by the skin and lungs [4,5]. In general, the salts of ionic alkyllead are considered to be more prevalent than the tetraalkyllead. Among the ionic alkyllead compounds, Me_3Pb^+ is the most common species and it usually constitutes more than 50% of the total organolead, according to the kind of additives used in European gasolines. Moreover, methyllead species are more stable and volatile than the corresponding ethylated compounds. For all these reasons, their determination is of major interest [6,7].

In the last few years the European Community Bureau of Reference Materials (BCR) has started a project to prepare certified reference materials for rain water and road dust based on the speciation of organolead, to sum up: Me_3Pb^+ [8–10].

The speciation and determination of ionic alkyllead compounds has been carried out by several methods which generally couple one specific de-

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tection system such as atomic absorption spectrometry, to one chromatographic system [11]. Among them GC–microwave induced plasma atomic emission spectrometry, and GC–inductively coupled plasma systems are notable for their sensitivity and power in this type of speciation analysis. However GC–MS is one technique with comparable sensitivity, which is more accessible and easier to handle, and which has been used on a few occasions [12,13].

On the other hand, in order to analyze ionic alkyllead compounds by chromatographic technics, one prior derivatization step is necessary to transform them to volatile and chromatographable species. The most common derivatization methods involve alkylation reactions that convert ionic species such as R_3Pb^+, R_2Pb^{2+} or RPb^{3+} to R_4Pb. As the additives in gasolines are tetraalkyllead compounds, where alkyl groups are mainly methyl or ethyl, the most used derivatization technics have been those that introduce one different alkyl group: butyl [12–15] or propyl [16], through a Grignard reaction. In order to carry out this derivatization is necessary firstly to extract the ionic alkyllead to an organic phase, which can be achieved by forming liposoluble complexes. This way, the derivatization becomes long and complicated, since it includes different steps such as acomplexation; extraction, derivatization (which is carried out under N_2 atmosphere) and further clean up and enrichment before the final analysis.

Both buthylation and propylation have been applied for derivatization, however the former is preferred, because the chromatographic separation of its derivatives is easier. The propylation has the advantage of reduction of retention times in the final chromatographic analysis.

Several papers have been published recently, which propose ethylation directly in aqueous phase using $NaBEt_4$ [2,3,17,18]. Even though this procedure does not permit the complete speciation since ethylated species are indistinguishable, it is so fast and simple that it can be an attractive alternative for speciation analysis.

The present paper shows the optimization of the ethylation process applied to an aqueous solution of Me_3Pb^+ in presence of Pb^{2+} in excess. The method has been applied to a rain water sample used in an interlaboratory exercise [8–12]. The whole process, as well as the individual steps, are compared to the alkylation procedure through Grignard reaction in organic media. Advantages and disadvantages of both methods are discussed.

2. Experimental

2.1. Reagents

Deionized water, further purified in a Millipore Milli-Q system, was used throughout.

The standard solutions were prepared with commercial pure solid Me_3PbCl supplied by Alfa Products.

Standard solutions of $EtMe_3Pb$ and Me_4Pb were prepared in hexane (Merck for residue analysis) with commercial solutions supplied by Associated Octel.

Sodium tetraethylborate ($NaBEt_4$) was obtained from Strem Chemicals.

The artificial rain water was prepared by dissolving in Milli-Q water the following high purity salts: $(NH_4)_2SO_4$, KCl, $CaCl_2 \cdot 2H_2O$, NaCl, $Mg(NO_3)_2$, and with HNO_3, all supplied by Merck (analytical-reagent quality).

2.2. Apparatus

A GC–MS Hewlett-Packard 5890 Series II with a 5971A mass selective detector were used. A SGL-1 capillary column of 25 m×0.25 mm I.D., 0.25 μm film thickness was used. The chromatographic conditions are shown in Table 1.

3. Procedures

3.1. Storage and dilutions

The concentrated standard solution and artificial rain water samples were stored in the dark at 4°C. The working standard and the water samples were diluted with artificial rain water on a daily basis. This artificial rain water was prepared with a mixture of different ionic salts. The ionic composition of this rain water is shown in Table 2.

Prior to analysis the water samples were diluted, resulting in four solutions with different concen-

Table 1
Chromatographic conditions

Column	Capillary SGL-1: 25 m×0.25 mm i.d.×0.25 μm						
Precolumn	2 m (empty)×0.25 mm I.D. fused silica						
Injection volume	2 μl						
Injection T	250°C						
Detector T	280°C						
Column temperature program	Initial T(°C)	time (min)	$Rate_1$	T_1 (°C)	$Rate_2$	Final T(°C)	time (seg)
	40	2.5	10	60	30	260	5
Solvent delay	2.7 min						
Carrier gas	Helium: 55 kPa of head pressure						
SIM mode	Group	Retention time (min)	Start time[a] (min)	m/z			
	Me_4Pb	2.93	2.70	223-253			
	Me_3EtPb	4.64	3.60	223-253			
	Me_2Et_2Pb	5.52	5.20	208-223-267			
	$MeEt_3Pb$	6.41	6.00	208-223			
	Et_4Pb	7.15	6.80	208-237-295			

[a] Time at which the detector begins to measure.

trations: 5, 0.5, 0.05 and 0.005 ng/g of Me_3PbCl and 12, 1.2, 0.12 and 0.012 ng/g of Pb^{2+} (inorganic lead in excess). The dilution factors were gravimetrically controlled.

3.2. Analysis of water samples

The scheme of the procedure including the reaction vessel is shown in Fig. 1. Different volumes (10–450 ml) of water samples were taken and placed in the reaction vessel (10, 25, 100, 500 ml were used) and were buffered with a potassium hydrogenphtalate–hydrochloric acid buffer solution at pH 4.0. Then an appropriate amount (0.5–20 ml) of 0.1 M EDTA, as masking agent for inorganic lead, was added. This was followed by the addition of a volume of hexane (0.5 ml) containing 20 ng/g of Me_4Pb as internal standard. The reaction vessel was closed with a septum and then 1 ml of a 0.8% $NaBEt_4$ solution was injected. The mixture was shaken for 5 min and set aside for another 10 min to enable phase separation. The hexane phase was collected with a pipette, placed in an autosampler

Table 2
Artificial rain water composition

Inorganic salt	Concentration (mM)
$(NH_4)_2SO_4$	30.0
KCl	5.0
$CaCl_2 \cdot 2H_2O$	12.5
NaCl	60.0
$Mg(NO_3)_2$	10.0
HNO_3	until pH 4.6

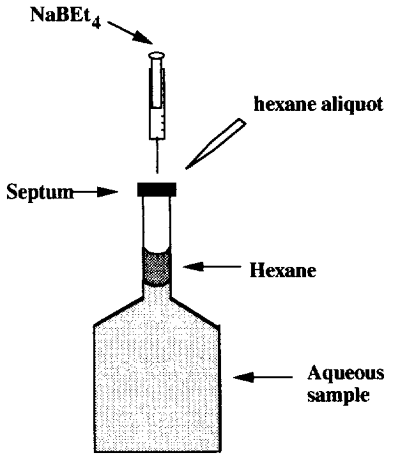

Fig. 1. Ethylation of Me_3Pb^+ in the reaction vessel.

glass vial and 2 μl of this final solution were injected in GC–MS-selected ion monitoring (SIM) mode for analysis.

3.3. Calibration

Quantitation of Me_3Pb^+ in rain water samples was carried out using a calibration plot obtained from standard solutions of $EtMe_3Pb$, which is the compound obtained by ethylation of Me_3Pb^+. Me_4Pb was used as internal standard. Relative concentration values against relative area counts were graphed to obtain the calibration plot.

4. Results and discussion

Speciation analysis of organometallic compounds usually needs a separation step in which the individual compounds can be separated, and specific detection. Most of the developed procedures use atomic absorption or emission techniques as detectors, and only a few of the published papers deal with mass spectrometric techniques even though the latter can be considered a specific detector for each compound [19–23]. In fact, mass spectrometry is focused on the individual structure of each compound. Based on the individual mass spectrum, characteristic ions can be selected for each compound, which makes the detection even more specific. The use of chromatographic techniques coupled with MS has the additional advantage of the availability of commercial instruments, with excellent sensitivity and without interface problems.

However, the common problem in speciation analysis is the transformation of ionic derivatives into volatile species. This conversion is usually carried out by Grignard reaction, in organic media. Another derivatization procedure which has been successfully applied to some organometallics is ethylation with $NaBEt_4$ [2,3,17,18]. As this derivatization reaction is performed in aqueous media, several parameters such as pH, $NaBEt_4$ concentration, time of reaction, volume of hexane and design of reaction cell, in which the derivatization–extraction is carried out, have to be optimized.

4.1. pH of reaction

Several buffer solutions ranging from pH 2–12 were applied to a standard solution of 12.5 ng of Me_3PbCl. Fig. 2 shows the percentage of the reaction obtained in each case against the pH values. As can be seen, the analytical signal (peak area) decreased gradually from pH 4. Consequently, pH 4 was considered as the optimum value. This result agrees with that mentioned in the literature [3].

4.2. $NaBEt_4$ concentration

As $NaBEt_4$ is unstable to both the light and the humidity, it was stored in an inert atmosphere prior to use, and fresh solutions were prepared in each case. Concentration values between 0.3% and 1.5% (w/w) were tested, but no significant differences were found in the analytical response. These results suggest that total ethylation is achieved even when the concentration of $NaBEt_4$ is slightly higher than stoichiometric ratio. But ethylation is not specific for Me_3Pb^+ and all the ionic species containing lead can be efficiently ethylated. This means that an excess of inorganic lead will also consume $NaBEt_4$. To prevent the consumption of reagent by other species of lead accompanying trimethyllead, a concentration of 0.8% of $NaBEt_4$ was considered as optimum value, which, together with the addition of EDTA as masking agent, was found to be efficient enough. However, working at pH 4, EDTA is not able to mask the Pb^{2+} quantitatively and for this reason, a peak corresponding to Et_4Pb was found. As chro-

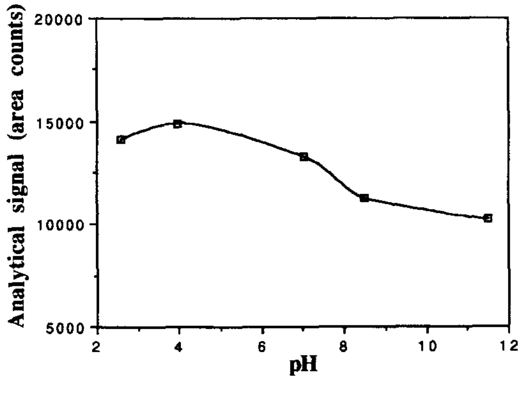

Fig. 2. pH Optimization.

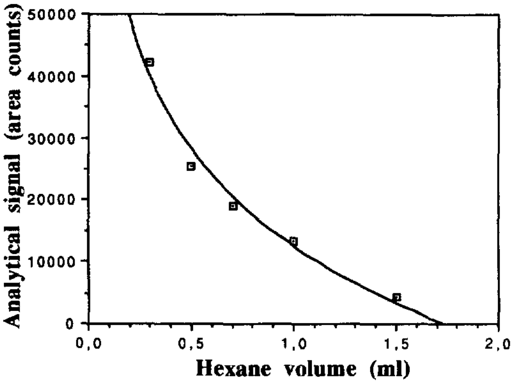

Fig. 3. Optimization of hexane volume.

matographic separation is very good, no problems of quantitation were found in these conditions.

4.3. Volume of hexane

As was mentioned above, both ethylation and extraction are carried out in the vessel at the same time. Tetraalkyllead species are non-polar and they are efficiently extracted into organic solvents [24], such as hexane. But this solvent has lower density than water and consequently it remains on the upper part of the vessel. Once the ethylation reaction is finished, the tetraalkyl species has to cross the water barrier to get into the hexane phase. It was found that when the vessel is shallow, the hydrostatic pressure is lower, and consequently the organic compound arrives efficiently at the hexane phase. On the other hand, if the upper part of the glass vessel is wide, it is very difficult to take a small volume of hexane. For all these reasons, two factors were taken into account: the cell in which the reaction would be carried out and the volume of hexane. Concerning the design of the cell, it was found that better results were obtained when wide round vessels with a long and narrow neck were used (Fig. 1).

The volume of hexane was investigated from 0.3–1.5 ml. Fig. 3 shows the results obtained. As can be seen, the peak area diminishes when the volume of hexane increases. This suggests that Me$_3$EtPb is efficiently extracted in 0.5 ml of hexane when the volume of aqueous sample is 100 ml. Higher volumes of hexane provide more dilute samples, and consequently, the analytical response is lower. Volumes lower than 0.3 ml hexane were impossible to handle quantitatively. For this reason, a value of 0.5 ml was considered as the most appropriate and both calibration and sample solutions were identically handled.

4.4. Reaction time

To get quantitative extraction of tetraalkyllead compounds, the mixture of aqueous solution and hexane phase was vigorously shaken. Different systems such as manual shaking, magnetic stirring and ultrasonic bath were tested from 5 to 20 min. Manual shaking for 5 min was shown to be the most efficient system, which can be explained by the homogeneous distribution of organic phase into the aqueous one. However, with magnetic stirring, the hexane remains in the upper part of the glass flask, and the contact between the aqueous and organic phases is very poor.

4.5. Analytical features

The calibration curve for Me$_3$Pb$^+$ was linear from 3.94 pg to 62.56 ng of compound injected into the GC column (Table 3). The correlation coefficient was 0.999–0.993.

Detection limit (expressed as three times the

Table 3
Analytical parameters for the determination of Me3Pb$^+$ in artificial rain water

	Linear limit (a)	Detection limit		Quantification limit	
		(a)	(b)	(a)	(b)
Ethylation method	3.94-62560.00	2.78	3.09	3.94	4.88
Buthylation method	7.20-199990.00	4.10	4.09	7.20	7.19

(a) Expressed as pg of compound injected into the column (volume 2 μl).
(b) Expressed as pg/g of compound in aqueous solution.

standard deviation of the background noise) for Me_3Pb^+ in rain water was 2.78 pg for the total mass injected, and the quantification limit (defined as the lower limit for precise quantitative measurements calculated by the calibration plot, in the whole method, and equivalent to ten times the standard deviation of blank measures) is 4.88 pg/g in water solution. Table 3 shows the analytical parameters for the determination of Me_3Pb^+ in artificial rain water, obtained in the ethylation method, which can be compared with those obtained in the buthylation method carried out by the same laboratory.

As can be observed, higher sensitivity and a lower quantification limit were obtained with the ethylation procedure compared to the buthylation through Grignard reaction [12]. This improvement can be attributed to the fact that ethylation with $NaBEt_4$ is a cleaner reaction than the Grignard reaction. Lower background noise and consequently a higher ratio of analytical signal–background noise as well as less sample handling, produce better analytical results. It can be emphasized that the combination of this simple reaction with the analytical system used, a GC separation with MS detection in SIM mode is an additional advantage and the whole system could be proposed as a powerful tool for speciation analysis.

According to the previous studies [12], some degradation compounds appear when Grignard reaction is applied to the same sample. This degradation has been described in the literature, and it is more important when the size of carbon chain is longer [15,20]. However, the derivatization with $NaBEt_4$, under the experimental conditions above described, does not produce degradation compounds.

When SIM mode is used in GC–MS, a very clean chromatogram is obtained, even selecting at least two characteristic masses for each compound, including $EtMe_3Pb$, Et_2Me_2Pb, Et_3MePb and Et_4Pb (Fig. 4). A peak of Et_4Pb appears in all the samples due to the presence of inorganic lead in the original samples, even after masking most of this Pb^{2+} with EDTA at pH 4. This peak was considerably lower than that obtained before the addition of masking agent. However, this inorganic lead does not produce interference either in the ethylation or in the final detection of Me_3Pb^+.

Blank samples were analyzed following the same procedure and only one peak corresponding to Et_4Pb was found. The size of this peak was similar to that obtained in both the calibration or real samples, confirming that the presence of this Et_4Pb is mainly provided by the reagents used. This behaviour has been already mentioned in the literature [12,15,20].

4.6. Recovery

In order to study the recovery of Me_3Pb^- in the whole process (ethylation and extraction), several spikes were prepared with rain water samples of different concentration, as was described in Section 2.

The concentration added was plotted against the concentration found, where the slope of the straight line is the recovery. The results obtained are shown in Table 4. According to these data, the average value of recovery for Me_3Pb^+ is 94.59±1.95%. This value implies that both the ethylation process and the

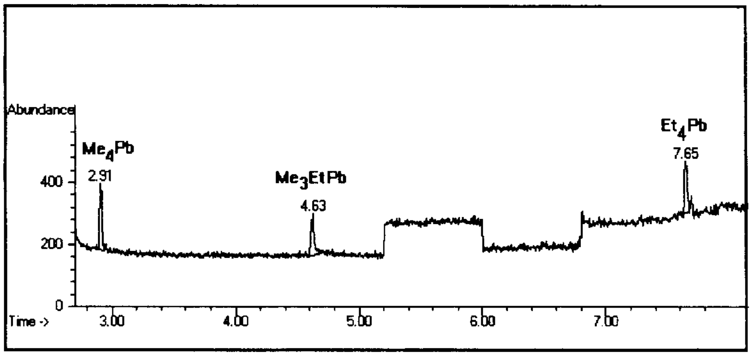

Fig. 4. Chromatogram of a sample of 7.79 ng of Me_3Pb^+ in rainwater, after ethylation with $NaBEt_4$.

Table 4
Recovery experiments according to the expression $y=ax+b$, where a=recovery value$\times 10^{-2}$, b=intercept and r=regression coeficient

a	b	r^2
0.9166	0.2715	0.995
0.9631	0.105	0.984
0.9580	−0.714	0.993
0.9565	0.140	0.998
0.9353	0.006	0.956

extraction were quantitative and free of interference from decomposition of the analyte.

4.7. Analysis of Me_3Pb^+ in artificial rain water samples

The developed method was applied to the artificial rain water samples prepared by BCR (CEE) for an interlaboratory study. These samples contain an excess of inorganic lead. The results obtained by all participants and by both ethylation and buthylation methods, are shown in Table 5. As can be seen, the accuracy and reproducibility of the proposed ethylation method is very good, even for the most diluted samples. Relative standard deviation values are much lower and faster with the ethylation procedure since the sample handling is lower.

5. Conclusions

From the study carried out, several conclusions can be pointed out as follows: (1) The ethylation procedure using $NaBEt_4$ is more sensitive than buthylation through Grignard reaction for the derivatization of Me_3Pb^+. Lower background noise as well as a lower number of degradation compounds produce a cleaner chromatogram in GC–MS-SIM mode and consequently, both the detection and quantification limits are lower too. (2) The ethylation procedure using $NaBEt_4$ is faster and simpler, with lower standard deviation because the extraction–derivatization combination is only one step. (3) The described procedure permits the determination of Me_3Pb^+. However, it is not possible to distinguish ethylated species such as Et_3Pb^+ from Et_4Pb or Pb^{2+} respectively, while buthylation can do that. (4) If extremely diluted samples have to be analyzed, the final extract can be concentrated under nitrogen atmosphere. This enrichment does not produce losses of analyte, as was previously described [23].

Finally, it can be said that the combination of the derivatization with $NaBEt_4$ in aqueous media, microextraction in hexane and direct analysis by GC–MS-SIM is a powerful tool for speciation analysis of organolead compounds.

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Table 5
Results of Me_3Pb^+ in artificial rain water samples (BCR)

Me3Pb$^-$ in the BCR samples (ng/g)	5.49	0.549	0.064	0.0064
Me3Pb$^+$ found by ethylation (ng/g)	5.78	0.582	0.067	0.0063
RSD (%)	3.53	5.96	2.14	2.46
Me3Pb$^+$ found by buthylation (ng/g)	5.98	0.81	0.083	-
RSD(%)	3.66	4.75	7.48	-
Results from the interlaboratory study (ng/g)	5.94-7.52	0.49-0.90	0.067-0.083	0.0074-0.0078
Number of participating labs.	9	8	5	2

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